

# Performance of a 1 kW-class PEMFC stack using TiN-coated 316 stainless steel bipolar plates

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## Abstract

To develop corrosion-resistant and low-cost metallic bipolar plates for polymer electrolyte membrane fuel cell (PEMFC), AISI 316 stainless steel was coated with TiN and the coated bipolar plates were applied to cell fabrication, in comparison with graphite and bare 316 bipolar plates. Initial performance of the single cells using graphite, AISI 316, and TiN/316 bipolar plates was 996, 796, and 896 mA cm<sup>-2</sup>, respectively, at a cell voltage of 0.6 V. By coating 316 stainless steel with corrosion-protective TiN layer, lifetime was also significantly improved. A 1 kW class short stack was manufactured using TiN-coated bipolar plates and operated for 1028 h.

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## 1. Introduction

For commercialization of polymer electrolyte membrane fuel cells (PEMFCs), it is required to significantly reduce the manufacturing cost of the fuel cell stack. Even though catalyst loading and membrane thickness have been lowered during the past decades, material cost still remains as a barrier for commercialization of PEMFCs. Among the PEMFC components, bipolar plates make the highest contribution to the stack cost; currently used graphite plates account for about 60% of the stack cost [1,2]. The cost target of bipolar plates for fuel cell vehicles was established to be \$ 10 kW<sup>-1</sup> [3].

As alternative bipolar plate materials, carbon composites and metal alloys have been extensively studied to meet the cost target [4–13]. Currently, both candidates are under consideration with their advantages and disadvantages as bipolar plate materials. In a previous study [14], carbon composite bipolar plates were developed and exhibited comparable ini-

tial and long-term performance to graphite bipolar plates. However, as pointed out in Ref. [14], mechanical strength of the carbon composite plates should be improved for scale-up of fuel cell stack. In this work, feasibility of metallic bipolar plates was studied as the second candidate.

As revealed in previous studies [4–13], the key issue in developing metallic bipolar plates is to prevent degradation of PEMFC caused by corrosion of bipolar plates leading to a decrease in electrical conductivity and contamination of membrane-electrode assemblies (MEAs). The proton conducting membrane used as an electrolyte of PEMFCs is typically composed of perfluorinated sulfonic acid polymer, which provides the bipolar plates with a very strong acidic environment under the PEMFC operating condition. Therefore, corrosion-resistant alloys such as stainless steels have been employed as bipolar plates of PEMFC. However, at present, performance and lifetime of the presented metallic bipolar plates are not satisfactory [4–13].

In this study, to develop a low-cost and corrosion-resistant metallic bipolar plate, surface of AISI 316 stainless steel was coated with TiN layer and characteristics and cell performance of the TiN-coated stainless steel bipolar plates were

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Table 1

Chemical composition of AISI 316 stainless steel used in this study (wt.%)

Fe	Balance
Cr	17
Ni	12
Mo	2.5
C	0.08
Si	–
Mn	–

examined in comparison with those of bare 316 stainless steel and graphite plates. Based on the results, a 1 kW class PEFMC stack was fabricated and its long-term performance was evaluated.

## 2. Experimental

### 2.1. Fabrication of metallic bipolar plates

To prepare metallic bipolar plates, AISI 316 stainless steel plates with thickness of 1.5 mm were chemically etched to form flow channels. Chemical composition of the alloy was given in Table 1. Then, surface of the plates were coated with TiN layer using hollow cathode discharge (HCD) ion plating method as follows; the chamber in which the etched plates were located was evacuated to  $3 \times 10^{-6}$  Torr and purged with Ar gas; a Ti target was evaporated at a discharge voltage of 260 V with being fed with N<sub>2</sub> gas at a flow rate of 160 sccm to form TiN layer. Operating pressure was  $6.3 \times 10^{-3}$  Torr. Thickness of the TiN layer was 1  $\mu$ m.

To fabricate bipolar plates with cooling channels for a stack, flow channels for gas and cooling water were formed on each side of a stainless steel plate, respectively. Then, two prepared plates were brazed facing the opposite cooling water channels. Finally, the united plate was coated with TiN layer as described above.

Before single cell tests, electrical contact resistance and water contact angle of graphite, 316 stainless steel, and TiN-coated 316 stainless steel were measured as described in detail in Ref. [14]. For comparison, graphite bipolar plates were prepared by machining flow channels.

### 2.2. Sing cell tests

For MEA preparation, catalyst ink for the electrodes was prepared by mixing the catalyst powders (40 wt.% Pt/C, E-TEK), Nafion solution, and *iso*-propyl alcohol. Then, the prepared catalyst ink was sprayed directly on the pre-treated Nafion 115 membrane with platinum loading of 0.4 and 0.7 mg cm<sup>-2</sup> for anode and cathode, respectively. The active electrode area was 25 cm<sup>2</sup>.

Single cells were assembled with the catalyst-coated membranes, wet-proofed carbon papers, gaskets, and the prepared bipolar plates. To operate the single cells, fully humidified hydrogen and oxygen gases were fed to the anode and

cathode, respectively. Stoichiometry of fuel and oxidant was 1.5 and 3, respectively. Operating temperature and pressure were 80 °C and 1 atm, respectively. Performance of the single cells was evaluated by measuring *i*–*V* curves using an electronic load (Daegil Electronics, EL 500P). To examine electrochemical resistance of the single cells, ac impedance was measured with an excitation voltage of 5 mV in the frequency range from 1 mHz to 10 kHz using an frequency response analyzer (IM6, ZAHNER). For the measurements, the oxygen electrode and the hydrogen electrode were used as a working and a counter electrode, respectively. The counter electrode also served as a reference electrode, since the overpotential at the counter electrode for the hydrogen oxidation or evolution reaction is negligible [11].

To investigate degradation of the bipolar plates, the single cells were operated at a cell voltage of 0.6 V and current density was measured as a function of operating time. After the long-term operation, contamination of MEA was analyzed by inductively coupled plasma and atomic absorption spectroscopy (ICP/AAS, MODEL ELAN 5000/MODEL 3030B/117 V).

### 2.3. Fabrication of a 1 kW class stack

A 12-cell short stack was manufactured using the TiN-coated 316 stainless steel bipolar plates. Thickness of the bipolar plates was 1.5 mm (without cooling plate) or 3 mm (with cooling plate). For the stack, the prepared catalyst ink was sprayed on carbon papers. Then, MEAs were fabricated by placing the catalyst-coated electrodes on both sides of a pre-treated Nafion 1135 membrane, followed by hot pressing at 140 °C and 200 kg cm<sup>-2</sup> for 90 s. The active electrode area was 240 cm<sup>2</sup>. Operating temperature was 60 °C. The experimental conditions not specified for stack fabrication were same as described above. The MEA fabrication conditions are summarized in Table 2.

## 3. Results and discussion

### 3.1. Material characterization

Generally, metals have good electrical conductivity. However, most of the corrosion-resistant alloys such as stainless

Table 2

MEA fabrication and operating condition for the single cells and for the 12-cell short stack using TiN/316 bipolar plates

	Single cell	Short stack
Catalyst loading (mg/cm <sup>2</sup> )	Pt/C Anode-0.4 Cathode-0.7	Pt/C Anode-0.4 Cathode-0.7
Membrane	Nafion 115	Nafion 1135
Active area (cm <sup>2</sup> )	25	240
Cell temperature (°C)	80	60
Operating pressure (atm)	1.0	1.0
H <sub>2</sub> /O <sub>2</sub> stoichimotry	1.5/3.0	1.5/3.0

steels have high electrical surface resistance due to the surface oxide layers that bring good corrosion-resistance to the alloys. As a bipolar plate material, an alloy with low surface electrical resistance and high corrosion-resistance is favored.

To evaluate electrical resistance of graphite, bare 316 stainless steel, and TiN-coated 316 stainless steel, contact resistance including bulk resistance of a bipolar plate material and two gas diffusion layers and interfacial resistance between the bipolar plate and the gas diffusion layers was measured since the contact resistance would have stronger effects on cell performance rather than bulk or surface resistance of the bipolar plate [14]. To simulate the fuel cell stack condition, the contact resistance was measured with applying various compaction pressures and shown in Fig. 1. With increasing compaction pressure to  $300 \text{ N cm}^{-2}$ , contact resistance of the materials decreased rapidly at low compaction pressures and then decreased gradually probably due to a decrease in interfacial resistance. At a given compaction pressure, contact resistance of 316 and TiN-coated 316 was almost same and higher than graphite. However, the difference was significantly reduced with increasing compaction pressure and, at stack assembly conditions, almost negligible; i.e., at a compaction pressure of  $180 \text{ N cm}^{-2}$ , contact resistance of graphite, 316, and TiN-coated 316 was measured to be  $30.23$ ,  $34.19$ , and  $32.71 \text{ m}\Omega \text{ cm}^2$ , respectively. These results show that, in the point of electrical contact resistance, 316 and TiN-coated 316 stainless steels can be applied to bipolar plates of PEMFC.

Surface energy of bipolar plates is another important factor affecting cell performance particularly at high current densities since water produced by the cathode reaction should be properly removed. Bipolar plates with low surface energy readily flood the cathode side of a cell [15]. To evaluate surface energy of the materials, water contact angle was measured. The lower the contact angle is, the lower is the surface energy of the material. Fig. 2 exhibits that water contact angle of graphite and TiN-coated 316 was almost same to be  $90^\circ$

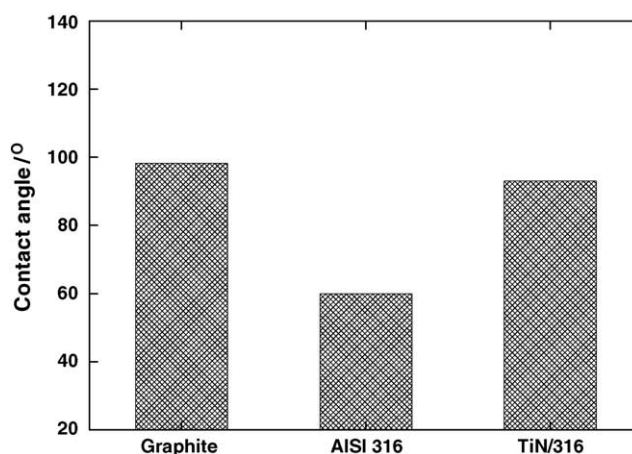


Fig. 2. Static water contact angle of graphite, AISI 316, and TiN/316 plates.

while that of 316 stainless steel was  $60^\circ$ . Those results imply that 316 stainless steel has low surface energy and more readily flood the cathode side than graphite and TiN-coated 316. In other word, by coating 316 stainless steel with TiN, performance decrease at high current densities that would be occur in a cell with bare 316 stainless steel bipolar plates might be repressed, as observed below.

### 3.2. Cell performance

To evaluate performance of the metallic bipolar plates, single cells were fabricated using graphite, bare 316, and TiN-coated 316 stainless steel bipolar plates. Fig. 3 shows initial performance of the single cells. Before the measurements, the single cells were operated for 24 h for activation. The metallic bipolar plates exhibited lower performance than graphite, probably due to the higher contact resistance, as revealed in Fig. 1. The low surface energy of bare 316 stainless steel could additionally reduce the cell performance particularly at high current densities. In addition, corrosion of the

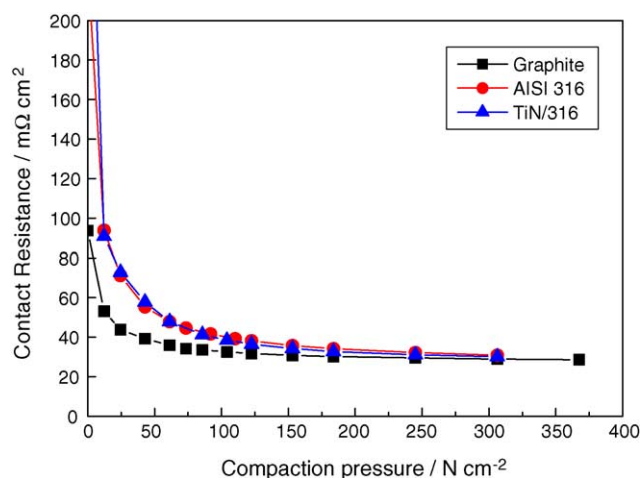


Fig. 1. Contact resistance of graphite, AISI 316, and TiN-coated 316 plates measured at various compaction pressures.

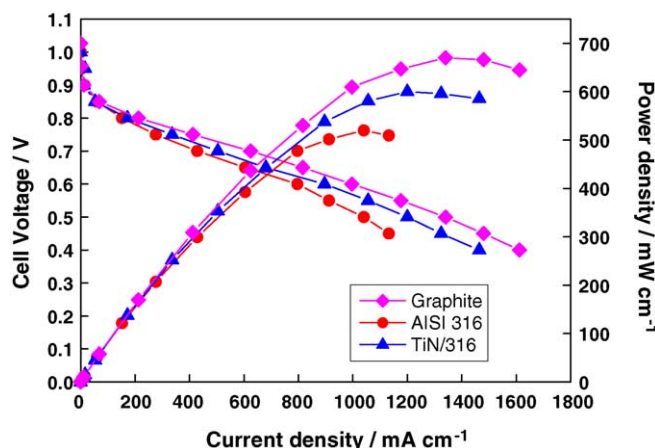


Fig. 3.  $i$ - $V$  curves for the single cells using graphite, AISI 316, and TiN/316 bipolar plates; operating temperature =  $80^\circ \text{C}$ ; operating pressure = 1 atm;  $\lambda_{\text{H}_2} = 1.5$  and  $\lambda_{\text{O}_2} = 3$ .

metallic bipolar plates during the activation process could reduce the cell performance. At a cell voltage of 0.6 V, the single cells employing graphite, bare 316, and TiN-coated 316 bipolar plates produced current density of 996, 796, and 896 mA cm<sup>-2</sup>, respectively.

To investigate Ohmic and charge transfer resistance of the single cells, ac impedance was measured at a cell voltage of 0.85 V after the measurement of  $i$ - $V$  curves presented in Fig. 3. The applied cell voltage was IR-corrected. Fig. 4 shows Nyquist plots for the single cells obtained from the impedance measurement. The Nyquist plots were semi-circular; the left point of intersection with the  $x$ -axis corresponds to the Ohmic resistance and the diameter of the semi-circle to the charge transfer resistance [16]. Ohmic resistance of the single cells using graphite, bare 316, and TiN-coated 316 bipolar plates was 5.57, 8.03, and 6.63 m $\Omega$  cm<sup>-2</sup>, respectively. The higher Ohmic resistance of the single cells employing metallic bipolar plates, particularly bare 316 bipolar plates, could be associated with contamination of the electrolyte membrane by corrosion of the alloys. Charge transfer resistance of the single cells showed the same tendency as Ohmic resistance; 30.7, 35.0, and 31.2 m $\Omega$  cm<sup>-2</sup> for graphite, bare 316, and TiN-coated bipolar plates, respectively. Those results reflect that, although lower than graphite bipolar plates, performance of 316 stainless steel bipolar plates could be improved by coating the surface with TiN layer.

In developing metallic bipolar plates, lifetime extension is another challenge in addition to improvement of initial performance since if corrosion of the bipolar plates occurs, performance decreases very rapidly. Lifetime of the prepared bipolar plates was evaluated by measuring current density at a cell voltage of 0.6 V as a function of operation time. Fig. 5 demonstrates that performance degradation of the single cell using graphite bipolar plates was negligible for 1000 h-operation. In contrast, with bare 316 and TiN-coated 316 bipolar plates, current density at 0.6 V decreased

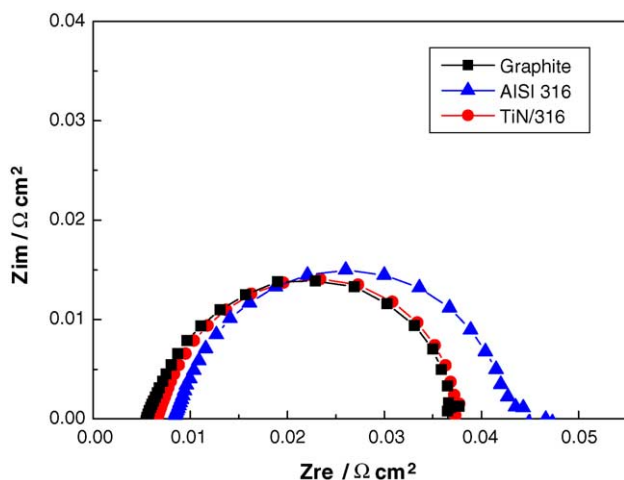


Fig. 4. Nyquist plots for the single cells assembled with graphite, AISI 316, TiN/316 bipolar plates at a cell voltage = 0.85 V; operating temperature = 80 °C; operating pressure = 1 atm;  $\lambda_{H_2}$  = 1.5 and  $\lambda_{O_2}$  = 3.

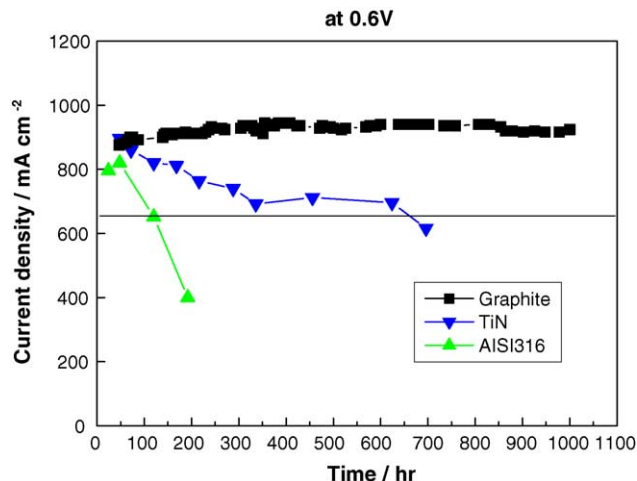


Fig. 5. Current density measured at a cell voltage of 0.6 V during long-term operation of the single cells using graphite, AISI 316, and TiN/316 bipolar plates; operating temperature = 80 °C; operating pressure = 1 atm;  $H_2$  = 1.5 and  $O_2$  = 3.

from 796 to 395 mA cm<sup>-2</sup> during 200 h and from 896 to 598 mA cm<sup>-2</sup> during 700 h, respectively.

During the long-term operation, ac impedance was also measured as shown in Fig. 6. Ohmic and charge transfer resistance of the single cells employing 316 bipolar plates increased more than two times during 200 h-operation while those of the single cell using TiN/316 bipolar plates increased only about 20% during 700 h-operation. For graphite bipolar plates, Ohmic and charge transfer resistance remained almost constant for 1000 h and was not given in Fig. 6. Those results could be attributed to contamination of the membrane and the electrode caused by corrosion of the bipolar plates.

Contamination of the MEAs was investigated by ICP analysis and the results were presented in Table 3 for the major elements of 316 and TiN-coated 316 plates (Fe, Cr, Ni, and Ti). For both bipolar plates, dissolution of Fe was dominant. In the MEA used with 316 stainless steel bipolar plates, the

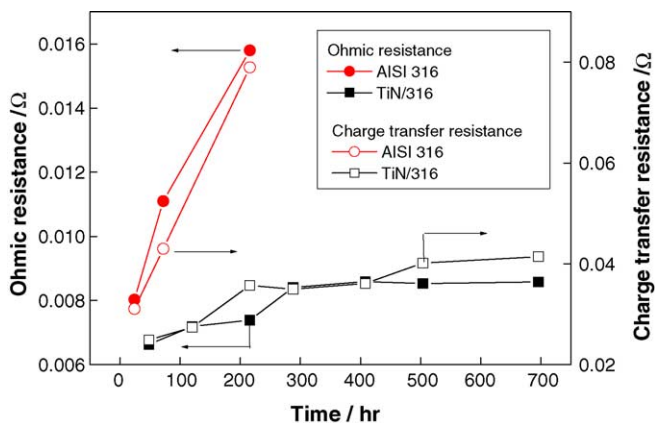


Fig. 6. Current density measured at a cell voltage of 0.6 V during long-term operation of the single cells using graphite, AISI 316, and TiN/316 bipolar plates; operating temperature = 80 °C; operating pressure = 1 atm;  $H_2$  = 1.5 and  $O_2$  = 3.



Table 3

Concentration of the metallic elements observed in the MEAs after long-term operation of the single cells using bare 316 and TiN-coated 316 stainless steel bipolar plates (wt.%)

Element	AISI 316	TiN/316
Ti	–	0.0033
Fe	0.87	0.12
Cr	0.038	0.038
Ni	0.33	0.018

much higher concentration of the metallic elements was observed than in that used with TiN-coated 316 bipolar plates although the operation time for 316 and TiN/316 bipolar plates was 120 and 700 h, respectively. Corrosion of metallic bipolar plates caused by the highly acidic PEMFC environment could result in contamination of MEAs which in turn leads to a decrease in ionic conductivity of the electrolyte membrane and to an increase in charge transfer resistance by poisoning of the catalytic layers [10,12].

All the results demonstrate that by coating 316 stainless steel bipolar plates with corrosion-protective TiN layer, performance and lifetime can be significantly improved. However, to replace the high-cost graphite bipolar plates with TiN-coated 316 stainless steel, it is strongly required to reduce the performance degradation.

### 3.3. Performance of a 1 kW class stack

Material characterization and single cell tests revealed a potential of the TiN-coated 316 stainless steel bipolar plates. Based on the results, a 1 kW class PEMFC stack composed of 12 cells was fabricated using the TiN-coated 316 bipolar plates with an active area of 240 cm<sup>2</sup>, as presented in Fig. 7.

Fig. 8 exhibits initial performance of the stack. Open circuit voltage (OCV) of the stack was 12.08 V. With lowering the voltage to 9.0, 7.2, and 6.0 V, the current increased to 45.0, 142.7, and 199.5 A, respectively. Maximum power was 1.18 kW at a stack voltage of 6 V and a current of 197.4 A. In a fuel cell stack, uniform performance of each unit cell is preferable. Fig. 9 shows the voltage distribution of the stack at OCV and at stack voltages of 9.0 and 7.2 V, revealing that voltage distribution in the stack was fairly uniform. Cell number was assigned from the gas inlet to the outlet. Standard deviation of the unit cell voltage was 7.7, 6.4, and 14.2 mV at OCV and at the stack voltages of 9.0 and 7.2 V, respectively. Voltage loss of each unit cell that was defined to be the difference between OCV and the cell voltage at 45 A was demonstrated in Fig. 10, ranging from 0.241 to 0.264 V. The voltage loss could result from non-uniform distribution of internal resistance (IR) of unit cells as shown in Fig. 11. The lowest and the highest IR value were measured to be 0.77 and 1.11 mΩ cm<sup>2</sup>. In addition, non-uniform distribution of the reactant gases from the gas inlet to the outlet and activation polarization of the electrodes could also contribute to the non-uniform distribution of unit cell performance.

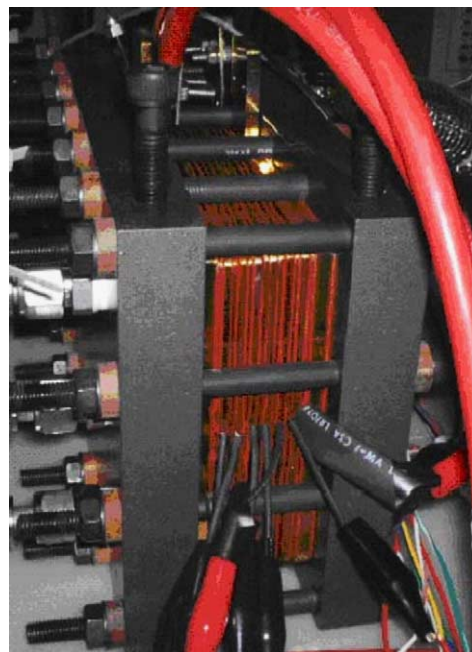


Fig. 7. The 12-cell short stack using the TiN-coated 316 stainless steel bipolar plates. Active electrode area was 240 cm<sup>2</sup>.

Fig. 12 shows the long-term performance of the stack. The stack was operated during 1028 h under a constant load of 48 A. The initial stack voltage was 9.0 V and lowered to 7.98 V at a degradation rate of 11% mV/1000 h, which is not an acceptable value for commercialization of fuel cell vehicles. However, investigation on degradation of each unit cell exhibits more promising results. Fig. 13 compares initial voltage and voltage at 1028 h of each cell measured at current of 48 A. Voltage decrease of cell 1, 2, 4, and 10 was about 10 mV while that of cell 3 and 12 was 120 and 180 mV, respectively, mainly contributing to the stack voltage drop. The lowest and the highest degradation rate were calculated to be 1.2%/1000 h (cell 1) and 31%/1000 h (cell 12), respectively.

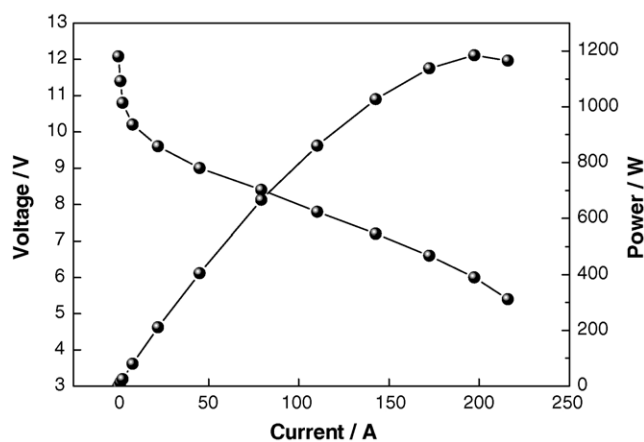


Fig. 8. *i*-*V* curves for the 12-cell short stack; active electrode area = 240 cm<sup>2</sup>.  $T_{\text{cell}} = 60^{\circ}\text{C}$ ,  $\lambda_{\text{H}_2} = 1.5$ ,  $\lambda_{\text{O}_2} = 3$ , and  $P = 1$  atm.

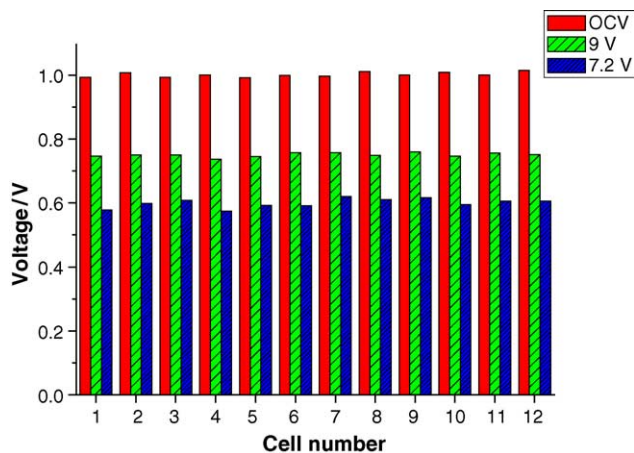


Fig. 9. Voltage distribution in the 12-cell stack at OCV, 9 and 7.2 V.

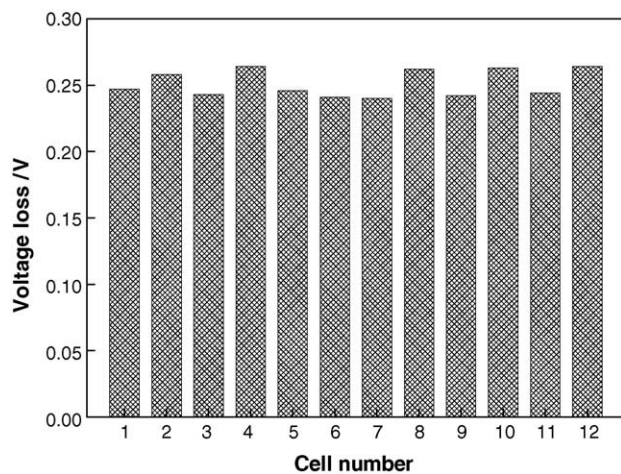


Fig. 10. Distribution of voltage loss of in the 12-cell stack calculated at a current of 48 A.

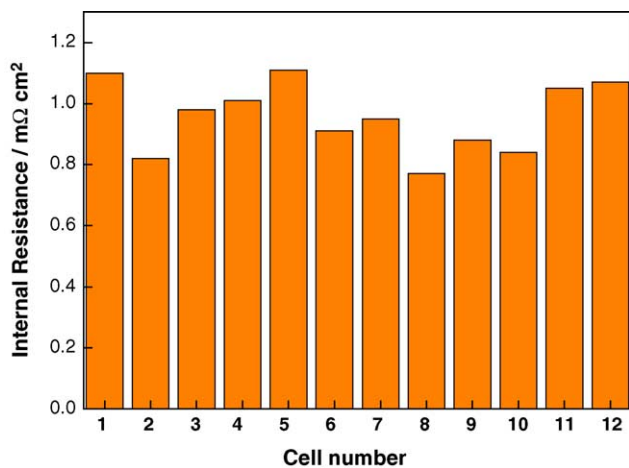


Fig. 11. Distribution of internal resistance in the 12-cell stack at OCV condition.

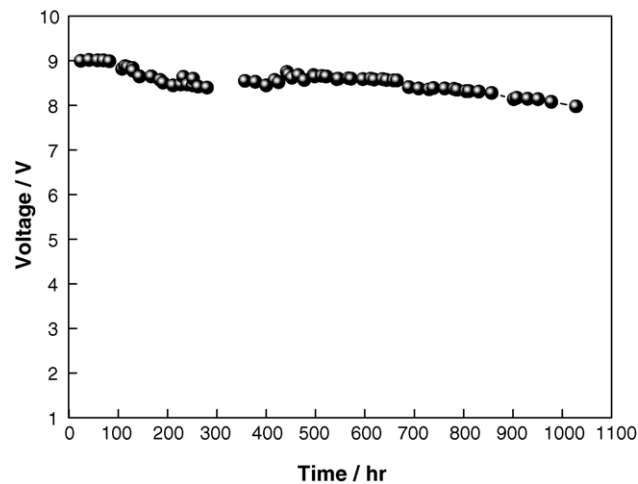


Fig. 12. Performance of the 12-cell stack during long-term operation at a constant load of 48 A.

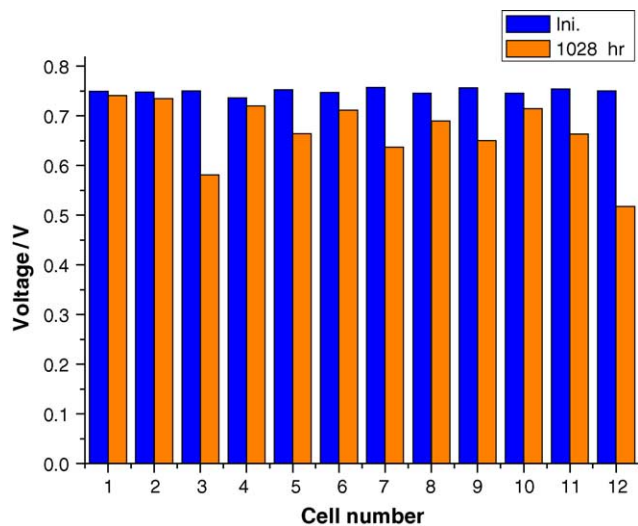


Fig. 13. Voltage change of each cells in the 12-cell stack under the continuous operation at 48 A.

Such a big difference in degradation rate could be attributed to the surface condition of the TiN-coated bipolar plates as well as non-uniform distribution of the reactant gases and produced water in the stack. It is well known that defects in corrosion-protective coating layer are crucial to localized corrosion [17]. Thus, it is expected that, by developing technologies for coating defect-free TiN layers and for distributing gases and water uniformly in the stack, lifetime of TiN-coated 316 stainless steel bipolar plates can be improved and applied to PEMFC stacks.

#### 4. Conclusions

TiN-coated 316 stainless steel was applied to bipolar plate for PEMFC, in comparison with graphite and bare 316

stainless steel. Electrical contact resistance and water contact angle of TiN-coated 316 were comparable with those of graphite. In single cell test, initial performance and lifetime of the TiN-coated 316 bipolar plates was significantly improved over those of bare 316 bipolar plates even though still lower than graphite bipolar plates. Dissolution of metallic elements such as Fe, Ni, Cr, and Ti from TiN-coated 316 bipolar plates into the MEA could increase in Ohmic resistance and charge transfer resistance of the single cell by contaminating the membrane and active catalytic sites. A 12-cell short stack was manufactured using the TiN-coated 316 stainless steel bipolar plates exhibiting the maximum power of 1.18 kW and operated for 1028 h at a current of 48 A. Degradation rate of the stack was 11 %/1000 h, and the lowest and the highest degradation rate of each unit cell were measured to be 1.2 %/1000 h (cell 1) and 31 %/1000 h (cell 12).

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